PNNL-SA-50369

Project Work Plan

Hanford 100-D Area Treatability Demonstration: In Situ Biostimulation for a Reducing Barrier

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1.0 Introduction

This work plan supports a new, integrated strategy to accelerate cleanup of chromium in the Hanford 100 Areas. The current treatment approach was driven by a series of interim action of records of decision (RODs), issued in the mid-1990s (EPA 1996, 1999). The RODs were concerned primarily with protection of the Columbia River, by the means of reducing the mass of chromium in the groundwater. These RODs called for pumping groundwater and treating the extracted water with ion exchange technology and one innovative technology, the in situ redox manipulation (ISRM) barrier. The discovery of two new contaminated groundwater areas has resulted in the need to improve and accelerate the approach to groundwater clean up at the Hanford 100-D Area. This proposal is one component of an integrated strategy for accelerating remediation of 100-D Area groundwater. This new approach will provide supplemental treatment upgradient of the ISRM barrier by directly treating chromium and other oxidizing species in groundwater (i.e., nitrate and dissolved oxygen), thereby increasing the longevity of the ISRM barrier and protecting the ecological receptors and human health at the river boundary.

The integrated strategy for the 100-D Area is summarized below:

- Immobilize chromium mass and reduce nitrate and dissolved oxygen concentrations in the southwestern plume upgradient of the ISRM barrier. A previous pilot-scale experiment at the 100-H Area, funded by the U.S. Department of Energy (DOE), has shown that injection of an organic substrate (polylactate) can stimulate indigenous microorganisms to reduce chromate and nitrate and deplete dissolved oxygen in the aquifer. This work plan describes treatability testing for applying in situ biostimulation as a potential low-cost, long-lasting means to provide treatment of chromate, nitrate, and oxygen over a large aerial extent upgradient of the ISRM barrier.
- Mend the ISRM barrier by injecting micron-size zero-valent iron into areas that show signs of breakdown. Coupled with upgradient bioremediation, longevity of the ISRM barrier will be substantially increased, leading to a final ROD.
- Increase the pace of groundwater remediation by deploying an electrocoagulation treatment system, which is capable of treating high flow rates and high concentrations of chromium in an expanded pump-and-treat system. The existing ion exchange technology cannot support the more aggressive treatment scheme required to accelerate remediation, and will be decommissioned when the new system is in place. The initial system will be online in 2007. After expansion of this new technology, the existing system will be shut down by 2010.
- Find the chromium sources that feed the groundwater plumes in the 100-D Area. This information will be used to remediate the sources, which will also accelerate cleanup and lead to a final ROD.
- Remediate waste sites along the Columbia River by 2012 through the River Corridor contractor.
- Continue to prevent future groundwater contamination by reducing artificial recharge, e.g., remove or repair leaking water lines.

In this integrated approach to chromium cleanup, three innovative technologies will be deployed in the 100-HR-3 Operable Unit. This approach is estimated to reduce life-cycle costs in excess of $40M and significantly accelerate chromium cleanup in the 100 Areas.

This work plan supports the accelerated cleanup (under the first bullet above) by performing a field-scale treatability test for bioreduction of chromate, nitrate, and dissolved oxygen. In addition to remediating a portion of the plume and demonstrating reduction of electron acceptors in the plume, the data from this test will be valuable for designing a full-scale bioremediation system to apply at this and other chromium plumes at Hanford.

2.0 Technology Description

2.1 Background

Limited field investigations and a qualitative risk assessment performed in the 100-HR-3 Operable Unit have established that hexavalent chromium is a groundwater contaminant of concern for ecological receptors in the Columbia River. An interim action ROD (DOE 1999) was issued for the 100-HR-3 groundwater Operable Unit in 1996 to address the chromium plume that was entering the Columbia River in the 100-D and 100-H Areas at levels exceeding the ambient water quality level of 10 ppb. The preferred alternative action in the interim action ROD was pump-and-treat technology, using ion exchange columns as the treatment technology. The 100-D Area aquifer has the highest concentrations of chromium on the Hanford Site (> 2000 ppb). Samples from aquifer tubes located near the river shore contain chromium concentrations at levels greater than 200 ppb (>20 times the aquatic standard, and >10 times the Remedial Action Objective of 20 ppb).

Chromium at varying concentrations was introduced to the soil and groundwater in the 100 Areas from a number of sources. The largest plumes were caused by disposing reactor coolant to surface basins. This coolant (with an initial maximum chromium concentration of about 700 ug/L) was treated with sodium dichromate to inhibit corrosion in the reactor cooling system. After passing through the reactor, the coolant flowed through large-diameter underground pipes to retention basins for thermal and radioactive cooling prior to discharge to the Columbia River. When fuel cladding ruptures occurred, trenches and cribs were used to dispose of the radiologically contaminated cooling water. Cooling system piping and retention basins leaked large volumes to the ground, creating substantial groundwater mounds and raising the water table over large portions of each reactor area. For example, the groundwater mound in the 100-D Area was 3 to 6 m higher than the ambient water table. These mounds dissipated following cessation of reactor operations.

Higher concentrations of chromium (>700 ug/L) were also introduced to the soil and migrated downward to groundwater through relatively localized areas. Leaks and spills of concentrated sodium dichromate stock solutions likely occurred where it was stored and handled. Chromic acid was used to decontaminate reactor equipment and was then disposed to French drains, cribs, and trenches.

In addition to the 100-D Area chromium plumes, oxidizing species, such as nitrate and dissolved oxygen, have a significant impact on ISRM barrier longevity. Groundwater nitrate concentrations upgradient of the ISRM barrier are about 60 mg/L over a wide spread area. Dissolved oxygen is currently being monitored in the wells up- and downgradient of the ISRM barrier. Monitoring data show that dissolved oxygen in upgradient wells were near saturation levels, ranging from 6.11 to 9.53 mg/L. Dissolved oxygen concentrations from wells within the treatment barrier show the effects of a strong reducing environment, ranging from 0.10 to 3.00 mg/L. Dissolved oxygen concentrations in compliance wells downgradient of the barrier ranged from 1.76 to 6.22 mg/L immediately down gradient of the treatment zone, while dissolved oxygen concentrations in two wells located slightly beyond the limits of the treatment zone ranged from 6.39 to 7.77 μg/L. These data show that dissolved oxygen in groundwater entering the ISRM barrier will have a significant impact on barrier longevity and that dissolved oxygen is replenished in groundwater as it travels downgradient of the barrier. It follows that any remedial approach that reduces dissolve oxygen and nitrate concentration upgradient of the ISRM barrier will increase barrier longevity.

2.2 Need for Supplemental Treatment upgradient of the ISRM Barrier

Although the primary purpose of the ISRM barrier was to immediately protect the Columbia River, additional remediation is required to address the high concentration portion of the chromium plume behind the ISRM barrier and to increase the longevity of the barrier, portions of which have been exhibiting signs of premature breakdown. The proposed method to accomplish this is to use in situ biostimulation to reduce hexavalent chromium and other oxidizing species (i.e., nitrate and dissolved oxygen) and establish a permeable reactive barrier that will continue to treat chromium, nitrate, and dissolved oxygen under natural groundwater flow conditions.

It is clear from monitoring data that the chromium plume is being fed by a continuing source of hexavalent chromium. Locating and remediating this source is a high priority task for the Groundwater Remediation Project. However, even after source remediation the 700-m-long plume will continue to be a threat to the river. Current modeling predicts it will take at least 40 years for the plume with concentrations > 20 ppb to move through the ISRM barrier, which is well in excess of the 10-year design life of the barrier.

2.3 Alternative Technologies Considered

The principal alternative technology considered was calcium polysulfide injection, which creates reducing conditions and results in the reduction of Cr(VI) to Cr(III). A primary concern associated with use of polysulfide is that the treatment would not be compatible with the use of the zero-valent iron treatment planned as part of the overall remediation scheme. Current plans are to inject zero-valent iron into several of the failing ISRM barrier wells. Another issue is the potential to adversely affect the aquifer and river by changing the groundwater chemistry. Among these are dissolved oxygen, oxidation-reduction potential, pH, iron, manganese, lead, and arsenic. The listed metals, which are naturally present in the aquifer materials, typically are mobilized in a reducing environment, but quickly re-precipitate when they reach an oxic environment.

Use of pump-and-treat technology was another potential alternative considered. However, because the southwest chromium plume is already being treated passively by the ISRM barrier, the use of this technology could be considered counter-productive because it could lead to reduction in the overall effectiveness and longevity of the ISRM barrier if not carefully designed. Studies have also generally shown that use of permeable reactive barriers have lower life-cycle costs than pump-and-treat systems.

Biostimulation is expected to be less aggressive and have a lower probability of geochemical impact than polysulfide while still achieving the desired goal of eliminating the high concentrations of chromate, nitrate, and dissolved oxygen upgradient of the ISRM barrier. Bioremediation can also be designed to sustain reduction of groundwater species over relatively long time periods via slow release substrates, buildup of biomass, and/or relatively inexpensive re-injection of substrates. Biostimulation is, therefore, the preferred alternative.

2.4 In Situ Biostimulation

In situ biostimulation has been extensively researched and applied for aquifer remediation over the last 20 years for various contaminants. In situ biostimulation, in the context of this project, is the process of amending an aquifer with a substrate that induces growth and/or activity of indigenous bacteria for the purpose of inducing a desired reaction. For application at the 100-D Area, the purpose of biostimulation is to induce reduction of chromate, nitrate, and oxygen to remove these compounds from the groundwater. Chromate can be biologically reduced to insoluble chromium (III) (e.g., Alam et al. 2006) and in situ chromate reduction has been recently demonstrated using polylactate as a substrate at the 100-H Area of Hanford (Hazen 2004; http://esd.lbl.gov/ERT/hanford100h/results.html). Nitrate can be biologically reduced using a variety of organic substrates including vegetable oil (e.g., Hunter 2001) and in situ nitrate reduction has been demonstrated at the Hanford site (e.g., Hooker et al. 1998). Biological nitrate reduction occurs as a stepwise process where the initial intermediate degradation product is nitrite. Under some conditions, nitrite concentrations can accumulate during nitrate reduction and nitrite needs to be monitored as a potential unwanted product of nitrate reduction. The final, desired product of biological nitrate reduction is nitrogen gas. Dissolved oxygen is readily reduced by a wide variety of bacteria in the presence of a wide variety of organic substrates.

All of these reductive processes induced by introduction of an organic substrate and the resultant biological processes creates geochemically reduced conditions in the aquifer (e.g., a low oxidation-reduction potential). Thus, the key groundwater monitoring parameters to evaluate continued chromate, nitrate, and dissolved oxygen reduction are the concentrations of these species, the concentration of nitrite, and the oxidation-reduction potential. Use of carbohydrate substrates proposed for this project should have minimal direct impact on groundwater chemistry in contrast to use of organic acid substrates. In addition to the organic substrate added to the aquifer, biomass that grows in response to the substrate is itself a substrate that can maintain reducing conditions and associated contaminant after the initial substrate amendment has been depleted. As some of the biomass dies, it is used as an organic substrate by other bacteria and thereby maintain reduced conditions.

3.0 Objectives

As part of the integrated strategy for the chromium plume in the 100-D Area, the overall goal for treatment of chromate, nitrate, and dissolved oxygen upgradient of the ISRM barrier is to reduce the electron acceptor flux to the ISRM barrier. This approach will extend the life-time of the barrier, thereby increasing protection of the Columbia River by immobilizing chromium in the aquifer before it reaches the river. To achieve this goal, chromate, nitrate, and dissolved oxygen concentrations need to be reduced over a relatively large aerial extent (~500 linear m of reactive barrier). Due to the potential for continuing chromate and nitrate sources, upgradient dissolved oxygen and a relatively long (700-m) chromate plume length, the upgradient treatment would also need to be effective over a long period of time (tens of years).

In situ biostimulation has been selected as a promising technique to meet the overall goals of the integrated strategy. This work plan outlines the approach for a treatability test to design and demonstrate that in situ biostimulation can be applied to meet the goals for upgradient treatment in the 100-D Area. The overall objectives of the treatability test are as follows.

- Demonstrate field-scale reduction of chromate, nitrate, and dissolved oxygen concentrations and the longevity of treatment to evaluate the effectiveness of the process at full scale.

- Demonstrate field scale application of biostimulation to evaluate implementability of the process at full scale.

- Determine the number of wells, type of substrate, operational strategy, and longevity for biostimulation such that costs for full-scale application can be effectively estimated.

Key biostimulation design parameters associated with these objectives include the radius of influence for injection of the substrate, mass of substrate that can be injected, biomass yield for the substrate, bioreduction yield for chromate, nitrate, and oxygen for the substrate and biomass, and the rate of substrate and biomass depletion. It is also recognized that site-specific hydrogeological characteristics influence the biostimulation design parameters and need to be determined to conduct the treatability test and for use in determining how the process will be designed for full-scale application.

4.0 Proposed Approach

To meet the goals for the integrated strategy in the 100-D Area (outlined in Section 1), chromate, nitrate, and dissolved oxygen concentrations need to be reduced over a relatively large aerial extent (up to 600 linear m of reactive barrier). Due to the potential for continuing chromate and nitrate sources, upgradient dissolved oxygen and relatively long (700-m) chromate plume length, the biostimulation approach would also need to remain effective, or be readily rejuvenated over a long period of time (tens of years). The biostimulation implementation must also consider the site setting where the plume is present in the relatively low permeability but heterogeneous (potential for high permeability channels) Ringold formation over a thickness of about 5 m. Using these primary considerations for full-scale implementation of biostimulation in the 100-D area, different approaches will be evaluated with respect to effectiveness, implementability, and cost. An initial evaluation of the primary alternatives is presented below. This evaluation was based on application of biostimulation in a reactive barrier 500-m long with one row of injection wells and for injection of substrate using a raw water supply (i.e., no groundwater recirculation) as a carrier. To assess the cost effectiveness of the biostimulation approach, rough cost estimates for a barrier duration of 40 years were compared to an estimate for maintaining the ISRM barrier through re-injection over a period of 40 years with an expected ISRM reinjection cycle of 10 years. At an approximate cost of $5M per ISRM re-injection, the baseline ISRM maintenance for 40 years is $20M.

Immiscible Substrates. The two primary options for immiscible substrates include polylactate solutions and emulsified vegetable oil solutions as discussed in the following paragraphs:

Polylactate Injection – The extensive literature and manufacture's information about polylactate (e.g., Regenesis 2001) suggests a likely radius of injection of about 3 m with about 1300 kg of lactate delivered within this radius for a 5-m thickness interval (~10 kg/m^3 aquifer). For a 500-m barrier, 84 wells would be necessary. Denitrification and reduction of chromate and dissolved oxygen depend on the longevity of the injected lactate, resultant fermentation products acetate, propionate, and hydrogen, and the biomass yield. Polylactate information suggests that a 2-year longevity for the barrier may be possible. Scoping calculations using these basic parameters were conducted. At a well cost of $75K, well installation capital is $6.25M. With a 2-year longevity, 20 injections are needed. We estimated $5K per well per re-injection for a total re-injection cost over 40 years of $8.3M. Thus, a rough total cost estimate for HRC is $14.5M. Use of HRC Advanced, which incorporates other longer-duration organic materials may extend the longevity and potentially offer a larger radius of injection. However, this product performance is considered similar to performance of Emulsified Vegetable Oil, which is considered below. For chromate, nitrate, and dissolved oxygen reduction, production of hydrogen, a design feature of HRC, is not necessarily needed and more simple substrates are likely equally suitable for the stimulation of these reactions. Use of organic acid substrate may also induce geochemical changes (as noted by the Lawrence Berkley Laboratory [LBL] effort assessing geochemical issues related to previous HRC tests).

Emulsified Vegetable Oil Injection – Injection of vegetable oil creates a reducing environment with a duration dependent on the rate of biological activity and the rate of oil dissolution. Literature information suggests a likely radius of injection of about 5 m with about 2700 kg of vegetable oil delivered within this radius for a 5-m thickness interval (~7 kg/m^3 aquifer). For a 500-m barrier, 50 wells would be necessary. Vegetable oil literature information suggests that a 5-year longevity for the barrier may be possible. Scoping calculations using these basic parameters were conducted. At a well cost of $75K, well installation capital is $3.75M. With a 5-year longevity, 8 injections are needed. We estimated $3K per well per re-injection (lees expensive substrate that HRC) for a total re-injection cost over 40 years of $1.2M. Thus, a rough total cost estimate for vegetable oil is $5M. Injection performance and distribution in the subsurface are strongly influenced by maintaining emulsification of the oil and the injection procedure. A key aspect of testing will be to confirm that the vegetable oil can be effectively distributed to an extent near what was estimated for the scoping study.

***Dissolved Substrates*.** There a multiple dissolved-phase substrates that can be used to biostimulate an aquifer. For the treatability test, molasses was selected as a representative substrate with a high solubility and low cost that has been applied at other sites for similar purposes. Molasses was preferred over use of an organic acid because of cost and the ability to inject a high quantity of substrate with minimal water chemistry issues. Dissolved substrates offer the potential for distribution over a larger aerial extent compared to non-aqueous phase substrates. In the Ringold formation, a well network would be expected to enable distribution of molasses over 15-m radius at concentrations around 10 g/L. Within this radius, about 5300 kg of molasses would be delivered for a 5-m thickness interval (~1.5 kg/m^3-aquifer). For a 500-m barrier, 17 wells would be necessary. Molasses would be relatively rapidly degraded and longevity would be partially dependent on decay of the biomass grown during molasses degradation. We conservatively estimated a longevity of 6 months for the scoping analysis (under natural gradient conditions about 3-4 month is required for groundwater to move from the upgradient to the downgradient edge of the treated zone), but potentially longevity may approach 1 year, especially if higher substrate injection concentrations are employed. Scoping calculations using these basic parameters were conducted. At a well cost of $75K, well installation capital is $1.25M. With a 0.5-year longevity, 80 injections are needed. We estimated $2K per well per re-injection (least expensive substrate, readily injected dissolved substrate) for a total re-injection cost over 40 years of $2.7M. Thus, a rough total cost estimate for molasses is $4M. Key parameters to assess in the design of a soluble substrate would include the biomass yield, appropriate injection concentration, and the associated longevity of the resultant barrier. Dissolved substrates, which have the potential to effect larger volumes, may also be more susceptible than immiscible substrates to small scale high permeability channels that may impact the uniformity of the substrate distribution around the injection well.

Based on the scoping calculations, emulsified vegetable oil and molasses substrates have the potential to offer significant cost savings over continued maintenance of the ISRM barrier by reducing the flux of electron acceptors to the barrier and thereby reducing the need for additional ISRM injections to maintain chromate reduction and protection of the Columbia River. Polylactate is less likely to provide savings. The previous polylactate testing at Hanford provided significant benefit in demonstrating that injection of an organic substrate into the aquifer can induce appropriate reducing conditions. For application at the 100-D Area, the testing will focus on emulsified vegetable oil and molasses as more appropriate substrates for this larger-scale application. The proposed approach in this work plan is to conduct separate single-injection field tests for both emulsified vegetable oil and molasses substrates.

The approach for the field test is to install two test cells consisting of an injection well surrounded by three monitoring wells (Figure 1). The test cells will be located such that an existing well can be used as an upgradient, unimpacted monitoring location. During well installation, sediment samples will be collected and used in laboratory microcosm studies to confirm that the substrates induce chromate, nitrate, and dissolved oxygen reduction. Field test operations will be conducted by injecting the substrate using a raw water supply as the carrier solution. Dissolved oxygen will be present in the carrier water, but the injection volume will displace chromate- and nitrate-contaminated groundwater during the injection. However, this displacement will be used to assist in evaluating the longevity of the treatment. Because chromate and nitrate will be initially absent in the treatment area, the injection and monitoring locations can be used to evaluate the breakthrough of chromate and nitrate at these locations as a means to assess when the reductive capacity has be exhausted. These data addresses the effectiveness and implementability objectives for the test. Distribution of the vegetable oil substrate will be assessed using geophysical methods and through monitoring of groundwater chemical oxygen demand at the monitoring locations just after injection. Molasses distribution will be assessed through monitoring of groundwater chemical oxygen demand and a conservative tracer at the monitoring locations during and just after the injection. These data and the operational aspects of the test will address the implementability objective for the test. The design and operational aspects of conducting the test in conjunction with the performance and distribution data will provide a basis to determine system scale-up and estimate cost for full-scale application; thereby addressing the cost objective of the test.

Through testing of the two different types of potential substrates (immiscible and dissolved), the testing will enable evaluation of how each substrate performs under field conditions (e.g., in the presence of field-scale heterogeneities) and will provide valuable information to assess the substrate best suited for application at the large scale necessary to meet the overall goals of the integrated strategy for the 100-D Area chromate plume.

The treatability test design will consider how to evaluate the key implementation issues for the biostimulation approaches selected for the treatability test in the context of the site setting. The test location will be targeted near the 1000 μg/L chromate contour in the 100-D Area (Figure 2). The target area will also be at least 200-300 m upgradient of the existing ISRM barrier so that the test can be effectively monitored without interference from the ISRM barrier and so that the test does not impact other technology efforts (e.g., iron particle injection) at the ISRM barrier.

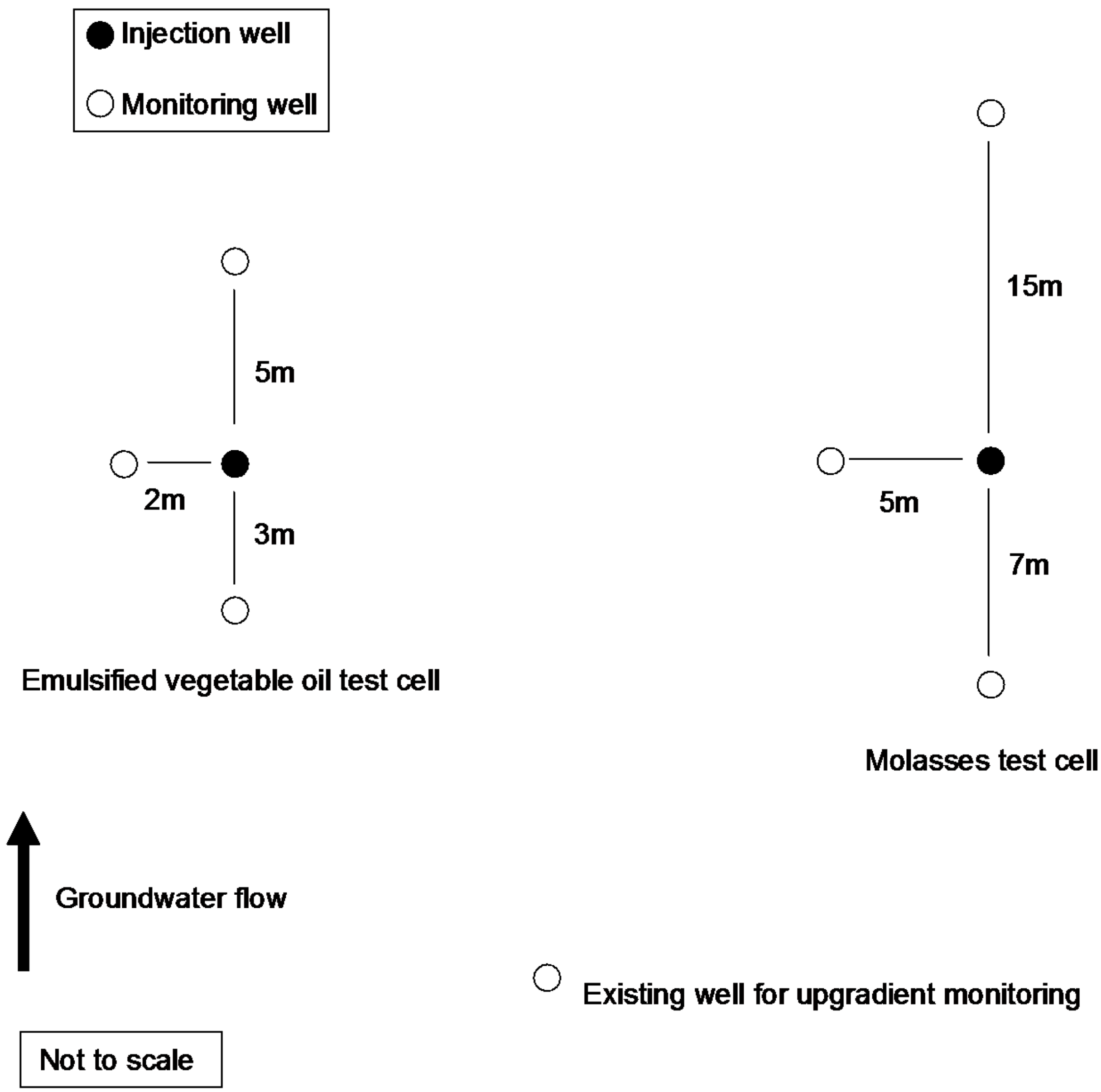


Figure 1. Conceptual Layout of Test Cells (to be finalized during the design process)

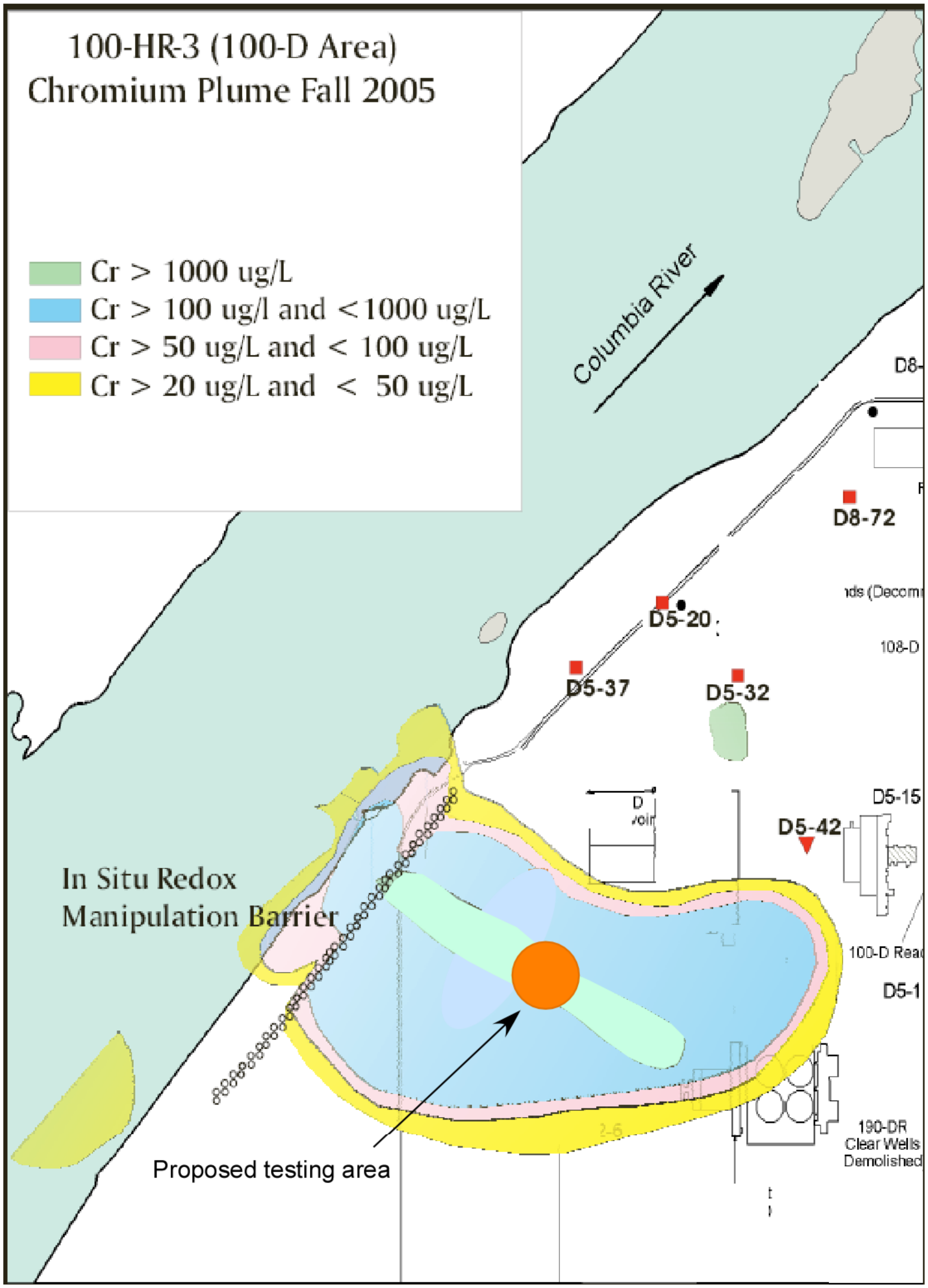


Figure 2. Proposed Test Area

5.0 Project Tasks

The overall scope of the project is to demonstrate a biostimulation process for reduction of chromate, nitrate, and dissolved oxygen concentrations in groundwater upgradient of the ISRM barrier. Field-scale treatability testing of biostimulation in the 100-D Area is divided into five tasks as follows: (1) Project Management, (2) Biostimulation Design Analysis, (3) Pilot-Scale Injection Test, (4) Performance Assessment Monitoring, and (5) Data Analysis and Reporting. Each task is described in the following sections. The project is designed to provide key field-scale treatability data that will support evaluation of the biostimulation process and scale-up design of a system that can meet the goals of the integrated strategy for the chromium plume in the 100-D Area.

5.1 Task 1: Project Management

Subtask 1a – Project Support. Plan, organize, and provide top-level guidance and direction for overall project performance. Also provide project-level cost and schedule control, tracking, and reporting. Coordinate the Columbia River Protection Supplemental Technologies Project work scope with DOE, Richland Operations, the Groundwater Remediation and Closure Assessment Project and the Office of River Protection, including participation in planning, peer reviews, and periodic project meetings.

Subtask 1b – Planning and Test Plan Preparation. This work element consists of developing both a laboratory-scale experimental approach and a field-scale treatability testing approach, and preparing planning documents. An experimental plan will be prepared at the beginning of the project to cover bench-scale laboratory testing. Once preliminary bench-scale testing results and site-specific characterization data are available, a field test plan will be prepared. Each plan will provide a description of planned testing activities, sampling and analysis methodologies, and data quality requirements.

Subtask 1c – Work Order to Fluor Hanford, Inc. Fluor Hanford, Inc. will review the treatability test plan and report; coordinate with other site contractors; provide operations site and representative support, regulatory, rad con and health and safety support; and assist in project coordination.

5.2 Task 2: Biostimulation Design Analysis

This work element will include two subtasks: (1) defining the hydrogeological and biogeochemical conceptual model of the Ringold formation in the zone targeted for the treatability test, and (2) initial design of the treatability test system.

Subtask 2.1 – Site Conceptual Model of Hydrogeological and Biogeochemical Conditions. This subtask will involve the evaluation of hydrogeological and biogeochemical conditions from existing wells and boreholes in the vicinity of the proposed treatability test site and incorporating this information into a working conceptual model of the site.

Subtask 2.2 – Initial Design of the Treatability Test System. The test design will describe the well network, injection equipment, injection protocol, and monitoring procedures for the test based on the data available prior to well installation at the site. The test design will also include description of the scale-up issues and how these are addressed in the test design and tools used to complete the design. The test design will be finalized in Task 3 to incorporate characterization information collected during the installation of the test site well networks.

5.3 Task3: Pilot-Scale Injection Test

This work element includes installation of a test site well network and associated site-specific characterization, bench-scale studies to support system design, finalization of the test design, substrate injection, and evaluation of the substrate distribution.

Subtask 3.1 – Well Installation and Site Specific Characterization. Based on the initial test design completed in Task 2, injection and monitoring wells will be installed at each of the two test cell locations. Data will be collected during well drilling and used to refine the hydrogeologic and geochemical conceptual model and finalize the substrate injection design.

Following installation of the well network, several hydrogeologic characterization methods will be used to obtain additional site specific information. These tests include hydraulic testing to obtain formation hydraulic properties and electromagnetic borehole flowmeter (EBF) testing to assess the vertical distribution of horizontal hydraulic conductivity (i.e., vertical heterogeneities). A conservative tracer injection test will be conducted in the vegetable oil cell using water withdrawn from the molasses test cell so that there will be minimal impact on the groundwater chemistry during the test. The tracer test will be used to further evaluate formation heterogeneities, to assess the aquifer hydraulic properties.

Subtask 3.2 – Bench-Scale Studies. Sediment samples collected during well installation will be tested for response to biostimulation. The basis for this testing is to assure that Ringold Formation gravels are similar in biostimulation response to the Hanford formation near 100-H Area where the previous test of polylactate was conducted. Laboratory microcosm tests will be conducted to assess the degradation of chromate, nitrate, and dissolved oxygen by both substrates and to assess biomass yield for molasses.

Subtask 3.3 – Final Design Analysis. Information from the field characterization effort will be used to finalize the injection strategy and test operational approaches for each substrate. The field test plan will be finalized as part of this subtask.

Subtask 3.4 – Substrate Injection. Substrate injections for each test cell will be conducted following the procedures in the field test plan finalized in subtask 3.3. Chemical monitoring will be conducted during injection to evaluate substrate distribution via monitoring of chemical oxygen demand, dissolved oxygen, pH, oxidation-reduction potential (ORP), specific conductance (SpC), and temperature (T). For the molasses test cell, conservative tracer will be co-injected with the molasses and monitored to assess molasses distribution and degradation during the injection process.

Subtask 3.5 – Geophysical Assessment of Emulsified Vegetable Oil Distribution. LBL will provide geophysical characterization to evaluate the radial distribution of the emulsified vegetable oil around the injection well.

5.4 Task 4: Performance Assessment Monitoring

Groundwater samples will be collected and analyzed to evaluate treatment performance. Hydraulic tests will be conducted following emplacement of the treatment zone and compared with pre-treatments values to assess the impact of treatment on aquifer hydraulic properties.

Subtask 4.1 – Groundwater Analyses. Primary performance monitoring will be via periodic spectrophotometric (Hach kit) and ion chromatography (IC) analyses to assess the temporal pattern of chromate and nitrate/nitrite concentrations, respectively, at each of the test cell wells. These data will be used along with coincident dissolved oxygen, ORP, and SpC measurements as the primary indicators for the longevity of the reductive zone induced by biostimulation. Concentration of conservative tracer within the molasses test cell will also be monitored to assist in evaluating the residence time of groundwater in the reduced zone under natural gradient conditions. Inductively coupled plasma – mass spectrometry (ICP-MS), inductively coupled plasma – optical emission spectrometry (ICP-OES) will be used to augment IC data to quantify aqueous cation, anion and trace metal concentrations before treatment and at two time points while the test cell is maintaining reducing conditions to evaluate the impact of biostimulation on groundwater geochemistry.

Subtask 4.2 – Post-treatment Hydraulic Testing. Hydraulic testing using slug interference techniques to minimize impact to the test cell will be conducted following emplacement of the treatment zone and compared with pre-treatments measurements to assess the impact of biostimulation and substrate injection on aquifer hydraulic properties. Specifically, pre- and post-treatment hydraulic responses will be compared to determine whether any degree of aquifer plugging.

5.5 Task 5: Data Analysis and Reporting

This work element consists of managing, compiling, and evaluating all of the data generated during the treatability studies and preparing a treatability test report. The final report will cover activities ranging from basic laboratory development work through a field scale demonstration of the technology. Findings presented in this report will form the basis of an evaluation of this technology for full scale implementation.

6.0 Assumptions

The following assumptions pertain to this scope of work:

- The project will start on or before September 15, 2006.
- A project specific Quality Assurance Plan (QAP) is required. This will describe the type of experiments, laboratory analysis, and the associated detection limits, duplicates, blind duplicates, and other quality assurance information.
- This treatability study will focus on the saturated zone and will not address potential contaminants in vadose zone porous media.

- The schedule shown in this proposal will be approved by DOE and the appropriate regulatory agencies.
- Fluor Hanford, Inc. will be able to provide drilling services for the project according to the proposed schedule.
- Investigation derived waste disposal services will be provided by Fluor Hanford, Inc.

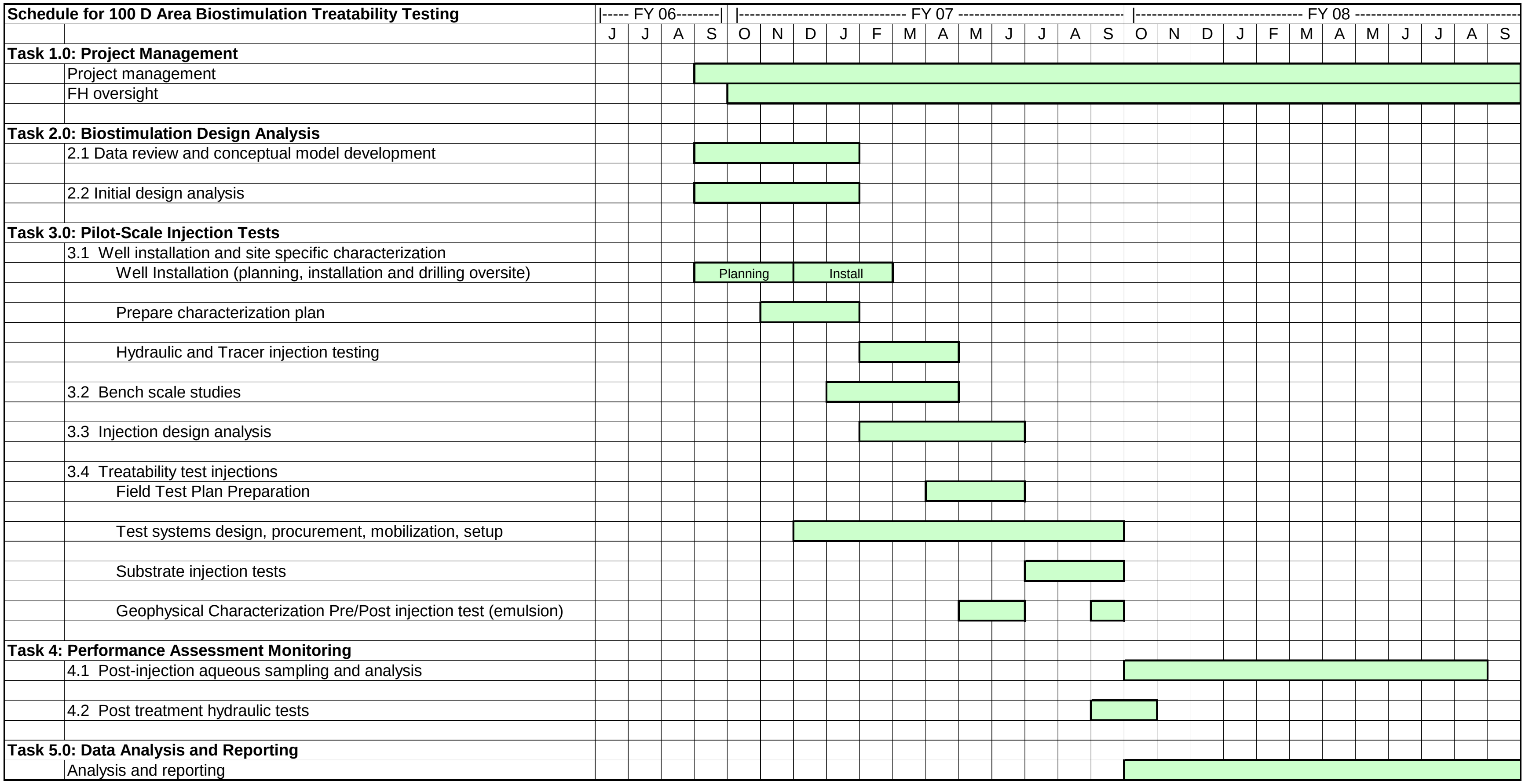
7.0 Schedule

A detailed schedule for the treatability test is shown in Table 1.

8.0 Budget

The total budget for this plan is estimated to be approximately $1,507,451.

Table 1. Schedule for the Treatability Test



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Appendix A

Response to Peer Review Comments

Target Plume/Area: **Chromium/Hanford 100D Area**
Previous Proposal Title: **Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection**

Summary:
The review panel felt that this was a significantly improved proposal compared to the earlier proposed calcium polysulfide treatment. The U. S. Department of Energy (DOE) should consider funding with the following caveats considered and addressed in developing the final work plan:

– Perform a more complete evaluation of alternatives and adjust the proposal as needed (e.g., justify the selected electron donor and well configuration).

Response #1: *With respect to selection of the electron donor, the authors agree that the original problem statement around which the subject work plan was developed (i.e., test the efficacy of using polylactate injection for accelerated bioremediation over the scales required to meet 100-D Area remedial objectives) was poorly posed and does result in an unnecessary level of technical risk. We concur that polylactate should not be preselected as the substrate of choice and that other potential substrates should be evaluated to determine which is best suited to full scale deployment at 100-D. The previous polylactate injection test at 100-H Area is important in that it demonstrated the viability of injecting substrate into the Hanford subsurface and effectively stimulating the indigenous microbes to deplete oxygen and reduce chromate. However, these positive results do not mean that polylactate is the best substrate for full scale application. This fundamental change in approach was adopted in the revised work plan, which includes a scooping evaluation of substrate options and plans for the evaluation of several electron donors as part of the treatability test.*

With respect to well configuration, the figures in question were a remnant of the original calcium polysulfide proposal and were not meant to represent proposed well configurations. Revised test cell figures have been included in the work plan.

– Reduce the Lab and theoretical components of the work and target a total cost of approximately $1000K. The reviewers felt that the initial effort should be a proof-of principle test, quickly applied in the field, to determine if a low-cost nutrient delivery system can maintain reducing conditions over reasonable time periods to enable a full-scale deployment.

Response #2: *The lab and design work proposed in the subject work plan were work elements the authors felt were important for determining how best to get polylactate distributed over distance scales much larger than is the typical polylactate application. Due to the relatively large depth to water and high drilling costs on the Hanford site, the authors feel that an industry standard application of this technology would not be cost effective. With the revision of the approach, laboratory testing has been reduced..*

– Develop technically based performance criteria that focus the objective of this effort and cost effectively monitor the action in combination with the other chromium response actions that are occurring upgradient and downgradient.

Response #3: *As indicated by the reviewers, the primary objective of this technology should be to provide for inexpensive, relatively long-term depletion of dissolved oxygen and nitrate over a scale sufficient to protect the ISRM barrier, with the reduction/precipitation of chromate as a secondary goal. The treatability test will be conducted at the appropriate scale for quantitatively assessing technology performance using the implementation approach most likely to be deployed during full scale treatment. The test would be used to assess the effectiveness of the selected implementation approach and substrate and develop an approach and cost basis for full scale deployment. An objectives section has been added to the work plan.*

The proposed approach is an appropriate part of a "defense in depth" concept for immobilizing chromium in the subsurface before it reaches the Columbia River. The proposed action is upgradient of the "to be repaired" ISRM barrier and downgradient of the suspected source areas (for which various ideas for locating and removing/treating are also proposed). The proposed project will produce reducing conditions and reduce dissolved oxygen, nitrate and Cr(VI) levels in the groundwater, thus extending the service life of the ISRM.

Response #4: *The authors agree. The selected test site should be far enough upgradient (or cross gradient) from the proposed ISRM iron amendment test site location such that performance assessment of the ZVI injections is not impacted.*

Technical Basis:

The project is generally based on established and appropriate science – specifically the use of lactate (in the form of polylactate) to release organic substrates (e.g., organic acids) to the groundwater. These act as electron donors with the primary objective of providing an appropriate biogeochemical environment for removal of electron acceptors from the system (thus increasing the longevity and reliability of the downgradient in situ redox barrier) and a secondary objective of Cr(VI) reduction to Cr(IV). This "systems" approach to addressing the plume is desirable and has the potential to provide an "optimum" solution – low costs for DOE, environmental protection, and minimized risks of collateral environmental impacts. Moreover, the proposal represents a proactive and appropriate response to the specific recommendations provided by the DOE technical peer review panel on the earlier calcium polysulfide treatment proposal. That peer review panel recommended consideration of a less aggressive yet longer lived electron donor to minimize potential collateral impacts and costs, and to maximize effectiveness in terms of key performance parameters such as lifetime of the action.

The project, as formulated, is somewhat inefficient, takes unnecessary technical risk, and lacks clear focus on the objective of the Columbia River supplemental funding:

Response #5: *The authors agree. See Responses #1 and #3 above.*

- While the presentation of the overall strategy and the "defense in depth" concept was good, there was insufficient work done in evaluating and comparing alternatives for this site (i.e., selecting the appropriate electron donor (Reviewers 1, 2, & 4), and in documenting that alternatives such as pump and treat are non-competitive (Reviewer 3)). Cost, longevity, deployability and other factors were insufficiently considered in this proposal. There was concern that polylactate may not meet the requirement for cost effectiveness and may present delivery challenges that would be difficult to overcome (Reviewer 2).

Response #6: *The authors agree that additional work is needed with respect to the selection of an appropriate substrate (see Response #1 above). However, documenting that alternatives such as pump* *and treat are non-competitive was not within the scope of this effort. Cost, longevity, deployability, and other factors are considered in the revised work plan as described in the new objectives section.*

– About half of the effort focuses on theoretical aspects of the migration of field-generated polylactate emulsions through porous media and then developing computer-based models of that process. This proposed work does not properly acknowledge or utilize the available literature on these topics and the proposed implementation does not appear as robust as commercially available emulsified electron donor products (Reviewers 2 and 4). This is not a basic research fund, it was implemented by Congress to provide supplemental funding, where needed, to improve the protection of the Columbia River in cases where the existing systems were not performing adequately.

Response #7: *See Responses #1 and 2 above.*

– Much of the design focuses on lab scale tests and modeling – this type of approach has had limited success in predicting and understanding system behaviors in complex heterogeneous subsurface settings such as the 100D Area of Hanford. This becomes important because there appears to be a bias in the proposal toward using minimal access and then lab testing / modeling (approx $900K) to prove that the system should work. The alternative, a field based paradigm with more robust access using a larger number of wells, has the potential to provide more reliable treatment at a lower cost (All Reviewers).

Response #8: *See Responses #1 and 2 above.*

– The proposed deployment method is not consistent with general practice and should be justified if used (Reviewer 4)

Response #9: *See Response #2 above. The approach has been revised and described in more detail in the new "Proposed Approach" section of the work plan. The revised approach and associated scoping evaluation of substrates does include consideration of general biostimulation practice.*

– More of the effort should be applied to monitoring field performance and to monitoring to assure that there are no substantive adverse impacts of the technology on the hydrology, the downgradient wall, or the Columbia River (Reviewer 4).

Response #10: *See Response #3, 4, and 9 above.*

Implementation Strategy:
The general feasibility of the process was demonstrated in an Office of Science EMSP project at the Hanford 100H Area in the Hanford formation. The project fits in well with the overall strategy for the 100-D Area chromium plume by providing an up-gradient treatment system to supplement the ISRM Barrier. Unfortunately, the proposal as currently structured is not reasonable and not practicable. Key issues are related to implementation and cost effectiveness as summarized below:

– While <u>limited</u> bench tests and modeling may be appropriate, these should not be the focus of the effort. A pilot field test is recommended as the primary method to ensure that heterogeneous fine-grained sediments from the Ringold formation will respond appropriately in terms of geochemistry, longevity, etc.

Response #11: *See Response #2 above.*

- A variety of electron donors are commercially available. As a starting resource, vendors' design guidance and recommendations should be used (Reviewer 1, 2 & 4)

Response #12: *The authors agree, see Response #1.*

- Costs are too high. Much of the detailed lab and theoretical evaluation of multiphase flow (notably, parts of task 3 including subtasks 3.1 to 3.5, and parts of task 2) may not contribute to the objective mandated by Congress for this funding. Specific suggestions on task and scope are provided by Reviewers 2 & 4.

Response #13: *The approach of the treatability testing has been revised and focuses use of the budget on conducting field testing for 2 types of biostimulation substrates. Cost for laboratory work has been significantly reduced.*

- While the proposal is generally well written, a diagram and scoping level description of the proposed implementation (maps with scales, a cross section, approximate number of wells, approximate amount of electron donor, etc.) should be included to aid in the review. The proposal contained few details on how the proposed project will be carried out in the field. How many wells will be used? Extraction wells? Monitoring wells? The information provided suggests only two wells will be used across the Cr(VI) contaminant plume. The reviewers were skeptical that this would result in a successful implementation even if such a marginal design could be justified by optimistic modeling based on small scale lab studies. (All Reviewers)

Response #14: *See Response #1 above. A scoping evaluation and a new "Proposed Approach" section have been added to the work plan include diagrams of the conceptual test cell design.*

Proposed Performance Metrics:

If the project were successful, it could improve the protection of the Columbia River by supplementing the ISRM Barrier. Targeted geophysical monitoring (to track changes and the presence of reduced conditions in the subsurface) accompanied by a groundwater monitoring strategy is a sound monitoring strategy. Please consider the following:

For the 100D systems approach, a focus on chromium reduction may not be appropriate as the oxygen and nitrate are responsible for the bulk of the oxidative potential of the groundwater, impacting the performance of the ISRM Barrier. Thus, performance metrics should be related to specific removal targets for electron acceptor (e.g., oxygen and nitrate) and treatment zone lifetime – these should be determined based on the necessary upgradient protection to ensure the performance of the ISRM barrier. The effective treatment zone may be better defined by geochemical footprints (and possible geophysics (e.g., SP) rather than trying to detect relatively low saturations of bulk electron donor in the subsurface. This is partially captured in the current proposal but needs to be clarified and emphasized.

Response #15: *The authors agree. The primary objective of this technology should be to provide for inexpensive, relatively long-term depletion of dissolved oxygen and nitrate over a scale sufficient to protect the ISRM barrier, with the reduction/precipitation of chromate as a secondary goal. The revised work plan includes new objectives and proposed approach sections and has been revised to clarify the focus of the testing.*